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Laser Pulse Desorption Under STM Tip-Cl Removal from Single Site on Si(100)

by

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Abstract

The desorption of pairs of chlorine atoms influenced by the tip of a scanning tunneling microscope is achieved at preselected sites on the Cl-saturated Si(100)-(2×1) surface using nanosecond laser pulse irradiation of the tip within the tunneling range. Bright features observed for the empty state topographic images after a laser pulse sequence are interpreted to be due to bare Si-Si dimers formed by laser induced desorption of two Cl atoms underneath the tip. The Cl desorption mechanism involves the enhancement of the sample - tip interaction due to laser pulse induced tip heating and tip expansion.

I. INTRODUCTION

Current lithographic techniques used in microelectronic technology are approaching the fundamental limits of their spatial resolution, and it is becoming more and more important to find new ways to overcome these limitations. One of the possibilities for creating extremely small structures with dimensions as small as the size of the atom is to use the scanning tunneling microscope (STM) as a tool for perturbing the surface. The strong local interactions achievable between the STM tip and the surface can lead to selective manipulation of the atoms underneath the tip.

Under usual tunneling conditions the close proximity of the tip does not lead to the local modification of surface structure. A standard way to enhance the surface - tip interaction is the reduction of the surface - tip separation or the application of short voltage pulses across the tunneling gap. This leads to an increase of the electrical field, and subsequently to an increase of the tunneling current, and possibly to local surface heating. All these factors can lead to local atom desorption from the surface or to local atom transfer from the surface to the tip or vice versa [1-3].

A different way to enhance the sample - tip interaction is the irradiation of the STM tip by very short laser pulses. The idea of irradiating the tunneling gap for the purpose of surface modification is not new [4-9]. However using laser pulses, single atom manipulation has been achieved only recently by transfer from the tip to the surface [10]. In these studies we have demonstrated that the irradiation of the tip by laser pulses leads to its transient thermal expansion, producing a very large transient current pulse across the tunneling gap in the μA

range. In a specific range of laser pulse energy ($\sim 12\mu\text{J}$ for 8ns pulses at 532nm) this leads to the deposition of single atoms from the tip apex [10].

Here we demonstrate the opposite effect in which the local desorption of chlorine atoms from a Si(100) surface site may be achieved by laser pulse irradiation of the tunneling gap.

II. EXPERIMENTAL

The experiments were performed in a UHV chamber with a base pressure of 2×10^{-11} Torr using commercial STM apparatus (Omicron). The Si(100) crystals (Virginia Semiconductors, P type, boron doped, $100\Omega\text{cm}$) were cleaned by high temperature annealing at $\sim 1410\text{K}$. After cooling the crystals were dosed with Cl_2 gas (Matheson, 99.999%) to saturation. The saturation Cl coverage was confirmed by measurement of the Auger peak ratio ($\text{Cl}_{\text{LMM}}/\text{Si}_{\text{LVV}} = 0.8$) [11, 12]. In addition, the STM image shows complete occupancy of all sites by Cl except the defect sites.

The second harmonic ($\lambda = 532\text{nm}$, $\text{FWHM} = 8\text{ns}$) of the pulsed YAG:Nd^{+3} laser (Continuum) was focused on the area of STM tip apex (spot diameter $\sim 250\mu\text{m}$) with an incidence angle of 80° with respect to the Si(100) surface plane. The laser pulse energy was measured in front of the UHV chamber window by a high sensitivity lithium tantalate detector (Newport).

A complete description of the sample preparation procedure and experimental setup used here is published elsewhere [10].

The dependence of the transient tunneling current on the laser pulse energy is shown in Figure 1. For both positive and negative sample bias voltages the results are similar. In Figure 1, for a reference current of 0.01nA and a positive sample bias of +2V, an exponential increase of transient tunneling current with the increase of laser pulse energy is observed. Fitted exponential dependence is shown as a solid line. This exponential dependence indicates that the mechanism at work involves tip heating and expansion in proportion to the laser pulse energy [10, 13], leading to the observed exponential dependence of transient tunneling current on laser pulse energy at the initial tip-sample separations explored here.

III. RESULTS AND DISCUSSION

The empty state images ($V_G = +2.5V$, $I = 0.05nA$) of the Cl-saturated Si(100) surface before and after laser pulse irradiation are shown in Figure 2. The image before laser pulse irradiation (Fig 2a) represents the first published STM image of the Cl-saturated Si(100) surface. It is known that Cl_2 adsorbs dissociatively on Si(100) with Cl atoms bonded to the dangling bonds of Si-Si dimers, preserving (2×1) surface reconstruction [2, 14, 15]. Despite the high concentration of defects we can clearly see the (2×1) structure of the surface produced by rows of the Si-Si dimers, each dimer site containing 2 Cl atoms. It should be emphasized that the center of the dimer row corresponds to the dark lines separating rows of bright oblong double features. The position of the Si-Si dimers containing chemisorbed Cl atoms can be assigned based on the images of the monoatomic step containing dimer rows on the top terrace running parallel with the step edge. Only one half of the oblong features is present there. The same effect was also observed on the clean Si(100) surface [16].

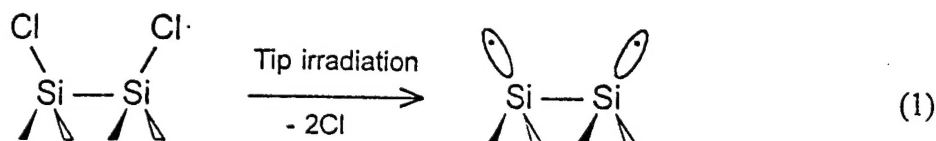
The main difference between images in Figs. 2a and b is the presence of nine bright features in Fig. 2b. These features were created in-between acquiring images in Figs. 2a and b during laser pulse irradiation of the STM tip while making a repetitive horizontal line scan (dashed line shown in Fig 2a). Along the line, 200 laser pulses were accumulated (laser pulse energy = $8 \pm 2 \mu\text{J}$) during the line scan of the STM tip ($V_G = 2.5\text{V}$, $I = 0.15 \text{ nA}$). For two hundred deposited pulses, the observation of nine bright features indicates that the probability of their formation during one laser pulse is about 5% under the conditions of this experiment. A change in the resolution of the STM before and after laser pulsing is often observed (Figs. 2a and b) and suggests that changes also occur at the tip apex during laser pulsing.

We have found that the probability of formation of bright dimers is strongly dependent on the laser pulse energy. No bright features were observed for laser pulse energy of $4 \pm 1 \mu\text{J}$, and the probability of their formation increased to $\sim 10\%$ per pulse for energy of $11 \pm 3 \mu\text{J}$. Unfortunately, for the high laser pulse energy we also observe another process, the deposition of the atoms from the tip apex as shown in our previous study on a clean Si(100) surface [10].

A detailed view of one of the features created by laser pulsing is shown in the left part of Figure 3a. From the schematic diagram of the imaged area (the right part of Figure 3a) it can be seen that the bright feature is centered symmetrically on the Si-Si dimer.

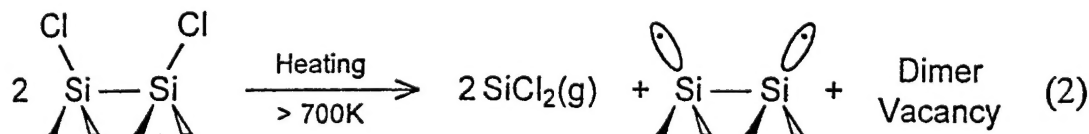
Figure 3b shows a constant current STM scan in two directions over the vacant Si-Si dimer site. Along Section A, a broad bright image is observed extending approximately across 5 Si-Si dimers. However along Section B, the bright image is symmetrically localized on a single Si-Si dimer.

We believe that the observed central bright dimer represents a bare Si-Si dimer pair after desorption of two Cl atoms as schematically shown in equation (1):



There is several reasons leading us to this conclusion:

- (1). Similar clean Si-Si dimers were observed as bright features also on the H-saturated Si(100)-(2×1) surface in the studies by Boland [17] and Shen et al. [3]. It seems that the main reason for much higher density of empty states of the clean Si(100) dimer site compared to the Si(100) dimer site saturated by adsorbate atoms is the presence of empty π^* orbitals [17, 18]. These empty orbitals are removed upon adsorption.
- (2). The thermal removal of SiCl₂ from a Cl-saturated Si(100) surface above ~ 700K also leads to the formation of empty Si-Si dimer sites at locations far from the SiCl₂ desorption sites. The loss of SiCl₂ species produces empty Si-Si dimer sites as well as dimer vacancy sites as required by the stoichiometry of the surface reaction. These empty Si-Si dimer sites are observed as bright features identical to those seen here by laser induced desorption of Cl atoms from a single Si-Si dimer site [19]. A schematic picture of this process is shown in equation (2):



There are two interesting questions connected to the observed laser-induced chlorine desorption: (1) What is the desorption mechanism? and (2) Why do pairs of Cl atoms desorb from the Si-Si dimers? The following observations help to answer the two questions.

- (1) Photoinduced desorption of Cl should exhibit a yield which extrapolates linearly to zero laser pulse energy. The threshold observed here for desorption of Cl is $4 \pm 1 \mu\text{J}$, making photoinduced desorption unlikely.
- (2) Surface heating might be expected to desorb Cl. However, the thermal desorption of $\text{SiCl}_2(\text{g})$ species rather than Cl_2 species is known to occur [14] forming Si-Si dimer vacancies on the surface. In addition the maximum possible heating effect due to the incident laser beam and to the transient current was theoretically estimated [10] to be too small to achieve the desorption temperature of $\text{SiCl}_2(\text{g})$ (more than 700K is necessary [14]). Therefore we exclude the thermal heating as the mechanism for Cl desorption here.
- (3) Field induced desorption in the STM configuration requires a field strength of the order of $1\text{-}4\text{V}/\text{\AA}$ [20, 21]. Based on Figure 1 we can determine that for laser pulse energies employed here the tip is in the tunneling regime and the tip-sample separation is more than $\sim 3\text{\AA}$ [22, 23]. In our experiments the Cl desorption is observed for sample bias as low as 1.5V. We estimate that the field strength is in this case less than $0.5\text{V}/\text{\AA}$ which is too low to cause field induced emission of the Cl from the Cl-saturated Si(100) surface.
- (4) Electron stimulated desorption (ESD) of adsorbed Cl. The energy of tunneling electrons is in the order of 1.5-2.5eV, that is much lower than is normally required for ESD processes [24]. However the effect of perturbation of the electrostatic field on possibly

operating repulsive ionic state is not clear and it is not possible to rule ESD mechanism out.

In the case of electron stimulated desorption the desorption of pairs of Cl atoms can be easily understood. It is known from the macroscopic observation of Cl^+ desorption that a much higher ESD cross section exists for low Cl coverages due to the removal of quenching effects due to Cl neighbor atoms [12]. Hence after desorption of the first Cl atom by the laser - STM combination, the local Cl coverage decreases, and the probability of ESD of the remaining Cl neighbor atom increases resulting in its efficient desorption.

- (5) Vibrational heating of the adsorbate due to inelastic electron tunneling was shown to be an effective mechanism for H atom desorption from H-saturated Si(100) surface [3]. It was theoretically demonstrated that this mechanism is effective in the case of adsorbates with high vibrational frequencies where the dissipation of vibrational energy in to the lattice phonon modes is ineffective [25]. In case of chlorine, the frequency of Si-Cl stretching mode is 600 cm^{-1} [14] that is very close to the lattice phonon frequencies ($\sim 500 \text{ cm}^{-1}$) [26] and we believe that the Cl desorption is not caused by this mechanism.
- (6) Chemical abstraction of Cl by the close approach of the STM tip is a common phenomenon involved in atom transfer processes at the tip - sample interface. This process can be enhanced by the electric field at the interface [27].

Based on the above discussion we favor direct chemical abstraction mechanism of Cl atoms assisted by the field. We believe that more detailed measurements of the Cl desorption

probability as a function of tunneling gap bias, sample-tip separation, tunneling current, and laser pulse energy will define the mechanism at work.

In conclusion, we have investigated the laser pulse induced desorption of chlorine atoms under an STM tip from a chlorine saturated Si(100) surface. Only the desorption of pairs of Cl atoms from Si-Si dimers was observed. It was found that the process is strongly dependent on laser pulse energy with 0, 5, and 10% probability of desorption of two Cl atoms per pulse for pulse energies of 4 ± 1 , 8 ± 2 , and 11 ± 3 μJ , respectively. The enhancement of the interaction of the tip with the surface is induced by laser pulse tip heating and tip expansion [10] likely with subsequent chemical abstraction of Cl atoms.

Acknowledgment

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Figure Captions

Figure 1 Dependence of the laser-induced transient tunneling current on laser pulse energy at constant reference tunneling current, $I_{ref} = 0.01$ nA and sample bias voltage, $V_G = +2$ V. The exponential fit of data is shown as a solid line.

Figure 2 The empty state topographic images ($V_G = +2.5$ V, $I = 0.15$ nA) of the same area of chlorine saturated Si(100) surface before (a) and after (b) the irradiation (200 laser pulses) of the STM tip in a line scan. The area repetitively scanned by STM tip during the laser pulsing is shown by a dashed line.

Figure 3 A detail view of the bright dimer feature created on the Cl-saturated Si(100) surface by laser pulsed irradiation of the tunneling STM tip (left part of the Fig. 3a). A schematic diagram of the scanned area of Cl-saturated Si(100)-(2×1) surface is shown in the right part of the Fig. 3a. The sections along the dimer row (Section A) and along the Si-Si dimer bond (Section B) are shown as 2-dimensional plots (Fig. 3b).

Dependence of Transient Tunneling Current on Laser Pulse Energy

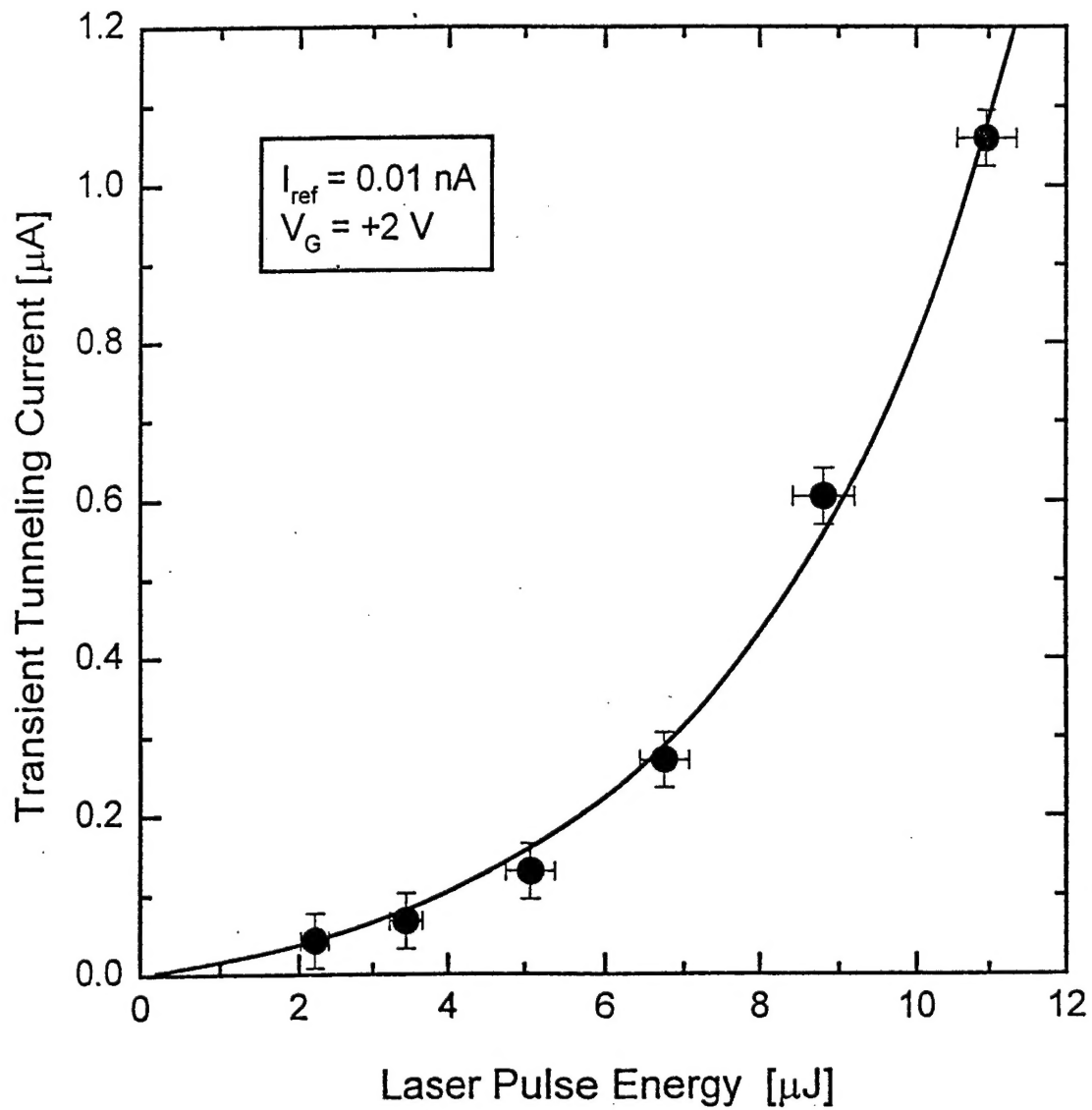


Figure 1
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STM Images of Cl Saturated Si(100) Surface before and after Laser Induced Removal of Cl from Single Si(100) Dimers

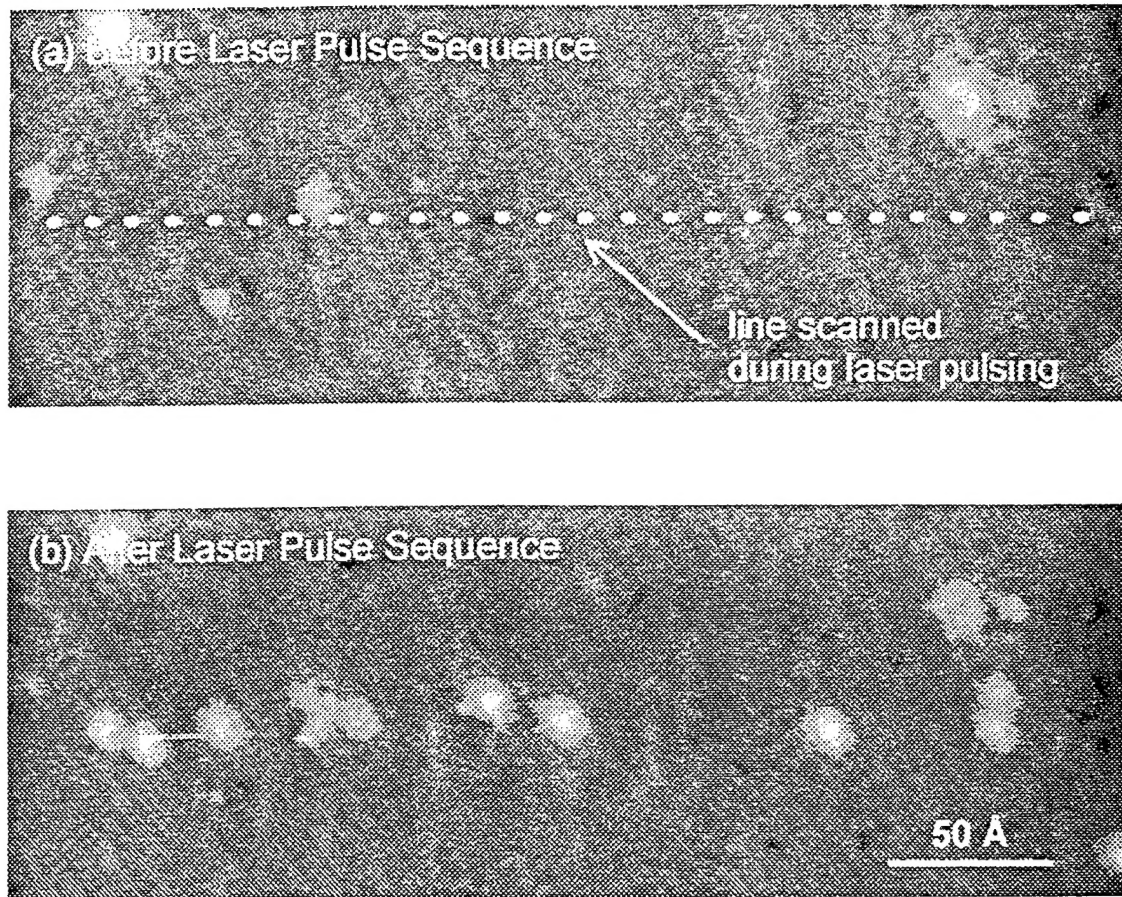


Figure 2
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Bright Dimer Feature Created by Laser Pulse Irradiation of Tunneling Junction - Cl Saturated Si(100)-(2x1) Surface

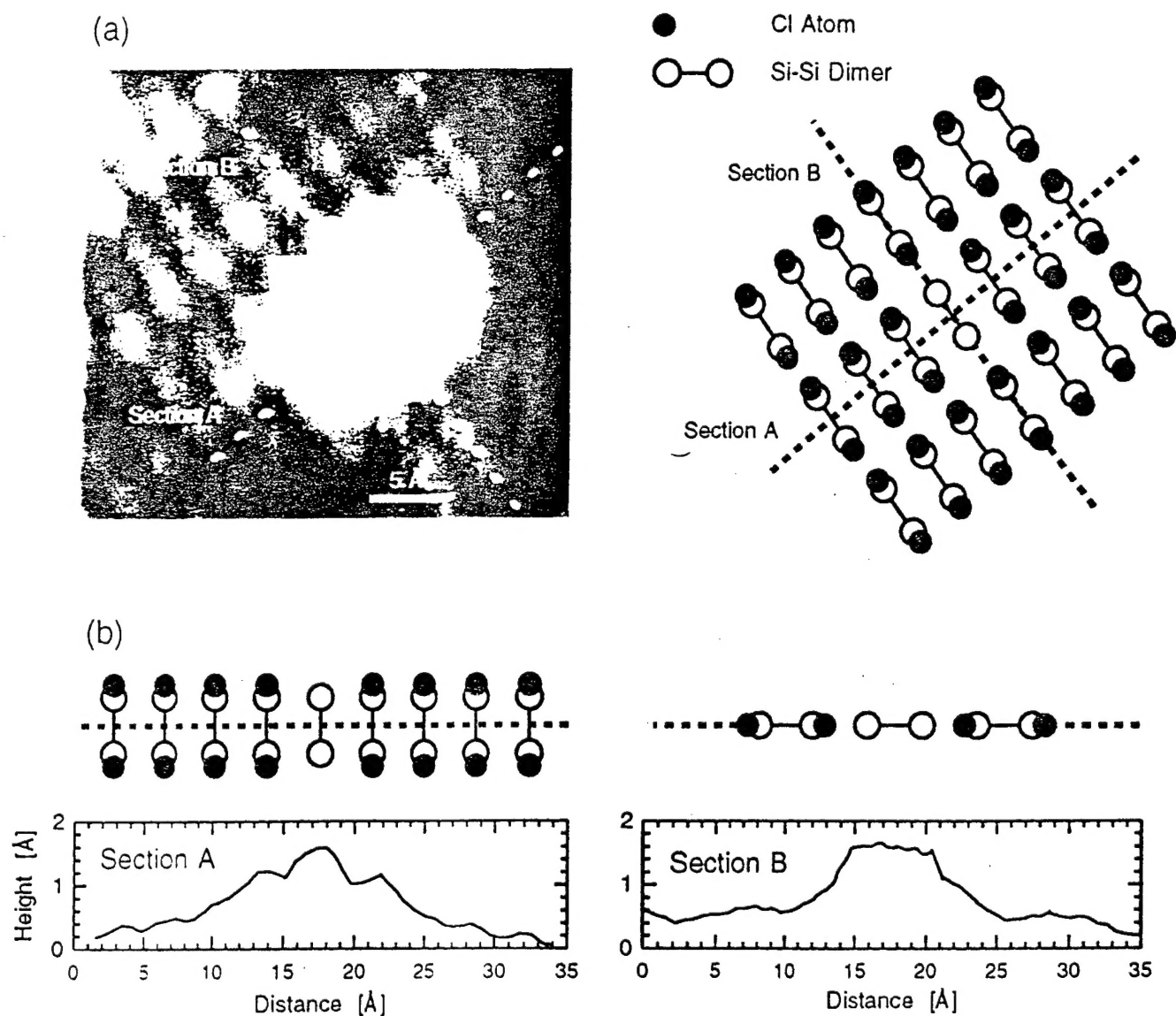


Figure 3
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